Polar anchoring energy and tilt angle measured by magneto-optical technique in nematic doped with ionic surfactant

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The surface anchoring of nematic doped with ionic surfactant is considered in comparison with an undoped one. Tilt angle of director at the substrates coated with a polymer orienting film was determined by the null method in rotating magnetic field. Frederiks transition in the magnetic field was chosen as a convenient technique for measuring the polar anchoring energy W_θ. The temperature dependences of the anchoring energy for various nematic cells have been obtained. The W_θ values for nematic doped with ionic surfactant are less than for the undoped one. The factors affecting the accuracy of the measurements are discussed. The accuracy is higher for thinner LC layers and for weak anchoring energy.

Keywords: nematic, ionic surfactant, tilt angle, anchoring energy, magnetooptics

1. Introduction

Liquid crystals (LCs) are the materials those properties can be controlled by the different external actions such as electric or magnetic field, temperature, etc. [1,2]. In the investigations and practical applications, LCs are usually placed between two substrates. The surface anchoring of LC molecules with substrates specifies the director configuration, which in turn assigns the bulk properties of the LC layer. Independent parameters characterising an interaction of LC with a surface are the tilt angle of director θ_0 (the angle

between a director and substrate surface) and polar anchoring energy W_θ. Besides, the temperature dependences of W_θ can provide important data about the liquid crystal/solid-surface interaction [3,4]. Various methods have been proposed to measure θ_0 [5] and W_θ [2] parameters. It has been found that the methods utilising the electric or magnetic field were the most effective [6]. One of the effective methods to measure θ_0 parameter is the magnetic null method in which the LC cell is rotated until its director is oriented parallel to the magnetic field. Determination of θ_0 is carried out by measuring the capacitance [7,8], optical transmission [9,10] or angle of total internal reflection [11]. The polar anchoring energy W_θ can be determined by measuring the threshold [3,4,12–14] or the saturation [12,15–17] fields of Frederiks transition in the electric or magnetic fields. Besides, the anchoring energy can be determined by measuring the birefringence and capacitance of the LC cell as a function of the applied voltage [15,18,19]. At present, the above methods of W_θ determination are widely used in the investigations [20,21] and have some advantages and disadvantages.

The influence of different additives on the response of LC materials at the application of external actions is of great interest to researchers. The additives in LC can lead not only to improving the response of the system, for example, dynamic characteristics, but also to the realization of new orientation-structural transitions in liquid crystals. For instance, the addition of the ionic surfactant in LC allowed to realise the electrically controlled changes of director configuration by the ionic modification of the surface anchoring [22–25]. In this method, the applied DC voltage induces the modification of boundary conditions due to the variation of the surface density of ions. Since the ions of surfactant are adsorbed at the interface, their influence on the polar anchoring energy is an important issue [26,27]. In this case the methods of W_θ measurement using the magnetic field are more suitable because the application of the

electric field can lead to the parasitic effects of ion redistribution [15]. This article is devoted to the determination of tilt angle θ_0 and anchoring energy W_θ of nematic LC containing ionic surfactant with polymer surface using magneto-optical methods.

2. Experimental technique

In the experiments, the sandwich-like LC cells were utilized. These cells consisted of two glass substrates covered by the polymer films of polyvinyl alcohol (PVA) which specify the planar surface anchoring for LC. Spin coater HO-TH-05 (HOLMARC) was used to form the polymer films on the substrates by spin coating. After that, the polymer films were uniaxially rubbed by Rubbing machine HO-IAD-BTR-01 (HOLMARC) to assign the uniform director orientation on PVA films. The substrates were assembled into cells so that the rubbing directions of polymer films at top and bottom surfaces were antiparallel. The cell gap thickness d was set using teflon films and measured by means of interference technique with spectrometer HR4000CG-UV-NIR. In one pair of cells the gap thicknesses were d_1 = 13.6 μm and d_2 = 13.9 μm while in other samples the thicknesses were d_3 = 5 μm and d_4 = 4.8 μm. The cells with d_1 and d_3 were filled with undoped nematic 4-pentyl-4′-cyanobiphenyl (5CB) while the cells with d_2 and d_4 were filled with 5CB containing 0.78 wt. % of ionic surfactant cetyltrimethylammonium bromide (CTAB).

Measurements of θ_0 and W_θ were made using the magnetooptical setup (Fig. 1). To determine θ_0 the beam of He-Ne laser *L*’ (LGK 7634, LASOS) with wavelength λ = 0.633 μm passed through a polariser *P*’, the LC cell *S*’, a crossed analyser *A*’ and was detected by a photodiode *F*’ (scheme 1 in Fig. 1). The signal from the photodiode was measured by a voltmeter. The angle between the rubbing direction of PVA films and polarisers was ±45°. LC cell was fixed at the rod between the poles of the electromagnet and adjusted so that the incident laser beam was perpendicular to the substrates. Rubbing direction of cell substrates coincided with the axial line of the electromagnet poles and lay in the plane of

rotation of the electromagnet placed on the stage *R*. The rotation angle Θ was set by a dial *G* with a diameter of 640 mm and changed in the range from -10 to +10° with a step of 1°. The magnetic field of about 18 kOe was applied to the sample at each value of angle Θ and the minimal change of the light intensity ΔI_{min} was found. In this case, the initial director orientation was approximately parallel to the force lines of the magnetic field and the value of angle Θ was equal to the tilt angle of the director θ_0.

[Figure 1 near here]

To determine W_θ the beam of He-Ne laser *L* (R-39727, Newport Corporation) with wavelength $\lambda = 0.633$ μm passed parallel to the axial line of the electromagnet poles through a polarizer *P*, the LC cell *S*, a quarter-wave plate *C*, an analyzer *A* and was detected by a photodiode *F* (scheme 2 in Fig. 1). LC cell was inserted into the constant-temperature cuvette. This cuvette was placed between drilled poles of the electromagnet so that the initial director orientation was perpendicular to the force lines of the magnetic field. The angle between the polarisation of incident light and LC director was equal to 45°. The temperature *T* in the cuvette was monitored by the copper-constantan thermocouple, and the magnetic field strength *H* was measured by the Hall probe. The stabilisation of the temperature and magnetic field was equal to ± 0.5%. The values of light intensity *I* and magnetic field strength *H* proportional to the signals from the photodiode and Hall probe, respectively, were measured by voltmeters, and the dependences *I* (*H*) were recorded automatically. The *H* value was varied in the range from 0 to 24 kOe, and the scanning rate was equal to 1 κOe/min.

In the initial state, the light intensity was set to zero at a certain temperature. For such adjustment of the optical system, the LC cell was firstly placed between polarisers

and the minimal light transmission was found by the analyser rotation. In this case, the semi-major axis of polarisation ellipse of light passed through the LC cell was perpendicular to the analyser. Then, the quarter-wave plate was placed between the sample and analyser so that the fast or slow axis of the plate was parallel to the analyser. It provided the linear polarisation of light after the quarter-wave plate. Finally, the zero light transmission was set by the analyser rotation.

The anchoring energy W_θ was calculated from the expression [28]

$$ctg\left(\frac{H_{th}}{H_{th}^{\infty}}\frac{\pi}{2}\right)=\frac{H_{th}}{H_{th}^{\infty}}\frac{\pi K_{11}}{W_{\theta}d}, \qquad (1)$$

where K_{11} is the splay elasticity constant of LC; d is the thickness of the nematic layer; H_{th} is the threshold value of magnetic field strength measured in the experiment; H_{th}^{∞} is the threshold value of magnetic field strength at $W_\theta \to \infty$. H_{th}^{∞} was determined as

$$H_{th}^{\infty}=\frac{\pi}{d}\sqrt{\frac{K_{11}}{\Delta\chi}}, \qquad (2)$$

where $\Delta\chi$ is the diamagnetic anisotropy of LC.

3. Results and discussion

In Fig. 2 the dependence of change of light intensity ΔI on the rotation angle of the electromagnet Θ is presented when the magnetic field is applied to the sample. The cell under study was filled with 5CB, and the thickness of the LC layer was equal to 13.6 μm. Rotating the electromagnet in the opposite directions, it is possible to find the intersection point of decreasing, and increasing parts of dependence ΔI (Θ) and this point corresponds to the tilt angle of director θ_0. From the data presented in Fig. 2, one can see that θ_0 is

about 1°. The same values of θ_0 were obtained for other investigated samples including the LC cells filled with 5CB doped by ionic surfactant.

[Figure 2 near here]

In the experiments on the measurement of the polar anchoring energy, the dependences $I(H)$ were obtained for different temperatures T of samples with LC layer thicknesses of 13.9, 13.6, 5 and 4.8 μm. The dependences *I(H)* for thinner layers of undoped 5CB and 5CB doped with ionic surfactant CTAB are presented in Fig. 3. One can see that ionic impurity does not significantly change the shape of *I(H)* dependences. For both samples the decrease of the reduced temperature T_{NI}-T, where T_{NI} is the nematic-isotropic transition temperature, leads to lowering the threshold field of Frederiks transition and simultaneous increasing the slope of curves $I(H)$ near the threshold. Similar dependences $I(H)$ at various reduced temperatures were obtained for the samples with LC layer thickness of 13.9 and 13.6 μm. In these cells the threshold of Frederiks transition was lower because of the thicker LC layers.

[Figure 3 near here]

The values of H_{th} were determined from the experimental dependences $I(H)$. Temperature dependences of threshold magnetic field strength H_{th} for LC cells with thicker and thinner nematic layers are presented in Fig. 4 and Fig. 5. One can see that the spread of experimental points for thicker LC layers (Fig. 4) is larger than for thinner ones (Fig. 5). In all investigated samples lowering the threshold field of Frederiks transition were observed when the reduced temperature decreased.

[Figure 4 near here]

[Figure 5 near here]

The obtained values of threshold magnetic field strength H_{th} were used to calculate the polar anchoring energy W_θ from expression (1). The values of H_{th}^{∞} were calculated from expression (2) where K_{11} and $\Delta\chi$ at certain reduce temperatures T_{NI}-T were taken from [29]. The temperature dependences of W_θ for the thinner LC layers of 5CB and 5CB doped with CTAB are presented in Fig. 6. One can see that the decrease of the reduced temperature leads to significant lowering the polar anchoring energy. The observed increase of slope of dependences *I(H)* in the threshold area (Fig. 3) is probably connected with this fact. The lower polar anchoring energy leads to the sharper change of director orientation in the central area of the cell when the value of the magnetic field increases [30] and, consequently, the intensity of light increases faster. The values of polar anchoring energy are in the range 10^{-2}–10^{-1} erg/cm^2 and these values are in good agreement with data presented in [31]. The values of polar anchoring energy for 5CB doped with ionic surfactant are less than for undoped LC. It might be connected with the fact that CTAB is the homeotropic surfactant and its addition in nematic leads to the weakening of the planar anchoring of LC molecules on the substrates. As mentioned above, the spread of experimental values of H_{th} for thicker LC layers was larger than for thinner ones. Utilization of threshold magnetic field strengths H_{th} presented in Fig. 4 and Fig. 5 leads to the even larger spread of points at the temperature dependences of polar anchoring energy W_θ. For that reason the reliable values of W_θ for samples with thicker LC layers were not obtained.

[Figure 6 near here]

To analyse the obtained results the possible factors affecting the accuracy of θ_0 and W_0 measurements were considered. Using the rotation of the electromagnet for determination θ_0 allows detecting the transmitted light more precisely because the possible errors connected with alternative rotation of the sample may be larger. The errors of the anchoring energy measurement are caused by the inaccuracies of H_{th} determination. Uncertainty in the experimental values of H_{th} can relate to the rounding of dependences $I(H)$ near the threshold area (Fig. 3). In [28] it has been shown that the sharp threshold of director reorientation is observed when the tilt angle of director on the alignment layers is equal to zero. In the case of a non-zero tilt angle the sharp threshold is absent. The conducted measurements of θ_0 by the magnetic null method have shown that the tilt angle was near to 1°. Such a value of tilt angle is not able to significantly distort the dependences $I(H)$. The rounding of dependences $I(H)$ near the threshold area can be also caused by the formation of an electric double layer arising from the adsorption of surfactant ions at the interfaces [26,27]. However the significant differences of $I(H)$ near the threshold area for undoped 5CB and 5CB doped with ionic surfactant have not been observed and this fact does not allow to suggest the existence of ordered near-surface layers.

The value of threshold magnetic field strength was determined as the point where the increase of light transmission from the initial zero value was observed. The small fluctuations of the temperature can also lead to the error of H_{th} because these fluctuations cause the change of the nematic birefringence Δn and consequently of the light intensity I. The intensity of light passing through the LC cell placed at angles ± 45° between crossed polarisers is determined by the expression [2]

$$I = I_0 \sin^2 \frac{\pi d \Delta n}{\lambda}, \qquad (3)$$

where I_0 is the intensity of the linearly polarised light incident at the LC cell, d is the thickness of the LC layer and λ is the wavelength of the incident light.

Figure 7 demonstrated the calculated dependence of I (Δn) when the temperature of the LC cell filled with 5CB is changed by 10°C. The calculation was performed using the expression (3) and the values of Δn at certain reduced temperatures were taken from [32]. One can see that the same change of Δn leads to the different variations of light intensity ΔI. For example, the change of Δn by 0.0014 leads to $\Delta I_1 = 0.1$ in the middle range of I values and $\Delta I_2 = 0.02$ for I values are near zero. For this reason, to increase the accuracy of H_{th} determination the quarter-wave plate was used in the optical scheme (scheme 2 in Fig. 1). Utilising this plate and analyser it was possible to adjust the initial light transmission to zero value and thus to increase accuracy.

[Figure 7 near here]

To analyse the experimental accuracy of W_θ determination, the dependences of W_θ on the reduced magnetic $h = H_{th} / H_{th}^{\infty}$ field for LC layers with d = 13.9 μm and d = 4.8 μm were calculated (Fig. 8). The calculations were performed using expressions (1) and (2). From the dependences one can see that in the case of rigid surface anchoring ($W_\theta \to \infty$) the value of reduced magnetic field tends to the unity and small error in the determination of threshold magnetic field strength leads to the significant uncertainty of W_θ. In the case of weak surface anchoring ($W_\theta \to 0$) the value of a reduced magnetic field tends to the zero, and the error in the determination of threshold magnetic field strength has a small influence

on the value of W_θ. A reliable determination of W_θ is in the range of small values of the anchoring energy. At the same time the accuracy of W_θ determination depends on the thickness of the LC layer. For example, the error in the determination of Δh_1 is equal to 0.008 leads to the uncertainty of polar surface energy $\Delta W_\theta \cong 0.08$ erg/cm^2 in thicker LC layer. However, in thinner LC layer the same uncertainty ΔW_θ is obtained when the error of Δh_2 is equal to 0.02. Thus, to increase the accuracy of W_θ measurement it is necessary to use thinner nematic layers and, consequently, higher magnetic fields.

[Figure 8 near here]

4. Conclusions

The surface anchoring of nematic 5CB both with and without ionic surfactant CTAB was tested in the cells whose substrates were coated with polymer orienting films. The tilt angle of the director θ_0 at the substrates and polar anchoring energy W_θ were measured in various LC cells. The angle θ_0 determined by a null method in rotating magnetic field was about 1°. The anchoring energy W_θ was measured using the threshold values of magnetic fields of Frederiks transition. Unlike the electric field technique, the use of a magnetic field avoids the redistribution of ions in the cell during the experiments. The temperature dependences of W_θ were obtained and they revealed that the decrease of the reduced temperature leads to lowering the polar anchoring energy. The W_θ values for 5CB doped with ionic surfactant were less than for the undoped one. This is because CTAB is a homeotropic surfactant, and its addition to the nematic leads to a weakening of planar anchoring specified by PVA orienting films. An analysis of the factors affecting the accuracy of measurements showed that the insertion of a compensator in the optical

scheme allows reducing the influence of temperature fluctuations. Besides, the accuracy of W_0 measurements is higher for thinner LC layers and also for weak anchoring energy.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 1. Scheme of magnetooptical setup. *L*, *L*' – He-Ne lasers; *P*, *P*' – polarisers; *E* – electromagnet; *S*, *S*' – LC cells; *C* – quarter-wave plate; *A*, *A*' – analysers; *F*, *F*' – photodiodes; *R* – rotating stage; *G* – dial. Schemes 1 and 2 are the optical schemes for measuring tilt angle θ_0 or polar anchoring energy W_θ, respectively.

Figure 2. Dependence of light intensity change ΔI on the rotation angle of the electromagnet Θ when the magnetic field is applied to the LC cell filled with 5CB. The thickness of the nematic layer is 13.6 μm. The arrow indicates the obtained value 1° of the tilt angle of director θ_0.

Figure 3. Dependences of light intensity *I* on the magnetic field strength *H* obtained at various reduced temperatures T_{NI}-*T* for the thinner layers of undoped 5CB (a) and 5CB doped with the ionic surfactant CTAB (b). Hereinafter, T_{NI} is the nematic-isotropic transition temperature. The LC layer thicknesses of 5CB and 5CB with CTAB are 5 and 4.8 μm, respectively.

Figure 4. The temperature dependences of threshold magnetic field strength H_{th} for the thicker layers of 5CB and 5CB doped with the ionic surfactant CTAB. Approximations are depicted by the solid lines. The LC layer thicknesses of 5CB and 5CB with CTAB are 13.6 and 13.9 μm, correspondingly.

Figure 5. The temperature dependences of threshold magnetic field strength H_{th} for the thinner layers of 5CB and 5CB doped with the ionic surfactant CTAB. Approximations are depicted by the solid lines. The LC layer thicknesses of 5CB and 5CB with CTAB are 5 and 4.8 μm, correspondingly.

Figure 6. The temperature dependences of polar anchoring energy for the thinner layers of 5CB and 5CB doped with the ionic surfactant CTAB. Approximations are depicted by the solid lines. The LC layer thicknesses of 5CB and 5CB with CTAB are 5 and 4.8 μm, correspondingly.

Figure 7. Calculated dependence of light intensity *I* on the birefringence of nematic Δn obtained from the expression (3). The LC layer thickness is d = 13.6 μm. Wavelength is λ = 0.633 μm.

Figure 8. Calculated dependences of the polar anchoring energy W_θ on the reduced magnetic field *h* for LC layers with thicknesses 13.9 and 4.8 μm.